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FLUORESCENT LIFETIME MEASUREMENTS
OF RARE EARTH ELEMENTS
IN GALLIUM ARSENIDE

THESIS

Danny J. Topp
Captain, USAF

AFIT/GEP/ENP/90-D-9

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THESIS

Presented to the Faculty of the School of Engineering

of the Air Force Institute of Technology

Air University

In Partial Fulfillment of the

Requirements for the Degree of

Master of Science in Engineering Physics

Danny J. Topp, B.S.

Captain, USAF

December, 1990

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Preface

The work I have done to complete this thesis has been enjoyable and very educational, a unique experience at AFIT. I would like to thank a few of the people who had a major part in ensuring my success.

Dr. Robert Hengehold corralled me to this thesis and over time I have come the realization that he has p obably done me one of the biggest favors of anyone in my short career as an Air Force officer. We worked very well together as thesis advisor and student. He was able to find time in his day for me, despite his full schedule as the Physics Department Head.

I would still be trying to align the dye laser if I had not had the expert skill and assistance of Greg Smith, Leroy Cannon and Bill Evans. They were happy to answer the smallest question or provide suggestions to ensure the experiment ran smoothly. I recommend that all three get hazard pay for having to put up with graduate students and their experiments.

The people who have gone through AFIT with me are a good bunch of folks. We support each other and help out when we can, and I couldn't have made it to graduation alone. Matt Rotondaro gets special mention for his help in Quick Basic programming. Thanks.

No Preface would be complete without mentioning the loving and supporting spouse. Thanks to my wife, Betty, for her patients and support. I will endeavor to be as supporting to her while she is attending AFIT and working on her thesis.

Finally, Thanks to my son, Bob, who spent his nights exploring the many ways a 3 1/2 inch disk will go into a disk drive. Thanks to Bob for helping me keep a rational perspective and providing needed hours of horse play.

Danny J. Topp

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Abstract

Lifetime measurements of the excited states of three GaAs semiconductors doped with the rare earth elements Erbium (Er), Praseodymium (Pr), and Thulium (Tm) has been studied using a pulsed nitrogen laser and germanium detector. The measurements were made with an experimental set up with a system response time of 0.34 μsec. A 330 milliwatt nitrogen laser with a wavelength of 3370 Å was used to excite intra $4f^n$ transitions of the rare earth elements. The rare earth impurities were implanted using ion implantation and conventional annealing. The implantation energies were 1 MeV for the Er and 390 keV for the Pr and Tm. The Er and Pr were annealed for 10 minutes with a Pr temperature of 750° and 680° for Er. The Tm was annealed for 15 minutes at 725°. The lifetimes of the excited states obtained were 361 ± 58 μsec for the 1.54 μm Er emission, 40 ± 7 μsec for the 1.39 μm Pr emission, and 8.7 ± 0.8 μsec for the 1.23 μm Tm emission. The measurements for the Er are comparable to previously reported lifetimes. The Tm and Pr lifetimes have not been previously reported, to the best of my knowledge. Attempts were also made to obtain PhotoLuminescent (PL) spectra of the samples, but system limitations prevented this. The three emissions strengths are shown in relation to one another and the Tm emission is found to be the strongest, with Pr next and Er the weakest signal strength of the three.

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I. Introduction

In recent years, the study of rare-earth ions in semiconductors has been one of strong interest because of their potential applications in opto-electronics. The rare-earth elements have unfilled 4f electron shells in their normal valence states, and generally form trivalent ions in a crystal. These trivalent rare-earth ions have various energy levels of the $4f^n$ electronic configuration, and these $4f^n$ energy levels are generally quite narrow, even when the ion is placed in a semiconductor. Thus, the emissions from the rare-earth elements in the semiconductors allow for sharp optical transitions, and accompanying narrow emission lines. In addition, the transitions are in the infrared at a minimum of the dispersion curve for fiber optic materials. These two factors combined in a solid state laser would provide higher data rates and less signal degradation for fiber optic communications.

This effort is part of a larger project within AFIT to study the dynamics that dominate the excitation and decay kinetics of photoluminescent emissions of Erbium (Er), Praseodymium (Pr), and Thulium (Tm) implanted in Gallium Arsenide (GaAs). The fluorescent wavelengths studied are 1.54 μm for Er, 1.1, 1.3, and 1.6 μm for Pr, and 1.2 μm for Tm.

An immediate goal of this study is to determine the decay lifetimes of the five emissions. A second immediate goal is to study the effects of the semiconductor doping and preparation process on the decay times. The long term goal of this project is to determine if an advanced semiconductor laser can be made with a wavelength

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associated with one or more of the rare-earth elements. My contribution to the effort will be to determine the fluorescent lifetimes of the 5 wavelengths at various temperatures. These fluorescent lifetime measurements are essential to understanding the mechanisms of energy transfer involved in the excitation and de-excitation of the rare-earth ions in semiconductors. Such an understanding will greatly enhance our ability to design and fabricate advanced semiconductor lasers for future Air Force applications.

The decay lifetime of the emissions are measured by exciting the electrons from the valance band of the semiconductor to the conduction band with a pulsed laser source. The majority of the excited electrons spontaneously return to the valence band, however, a few of these electrons transfer their energy to the energy levels of the rare-earth elements. The resulting emissions are very weak and have very narrow linewidths. The challenge of this project is to detect these very weak emissions, and measure their fluorescent lifetimes.

II. **Background**

2.1 Semiconductors

A discussion of semiconductors and their unique crystal properties is needed for a complete understanding of this experiment. The interaction between the crystal electric fields and the individual atomic electron shells determine the linewidth and decay time of each emission. This section is a condensation of material presented in McKelvey,(1) and provides the essential theory of semiconductors.

2.1.1 Band Theory When crystal structures form in a material, energy levels are formed into energy bands. these energy bands determine the allowable energy levels of the electrons. The highest level of the bound electrons is the valence band, these can interact with unbound electrons. The other unbound electrons reside in a conduction band as free electrons. Between these two bands is a forbidden energy region, electrons in the crystal can not exist at energies in this region.

The material type is determined by the presence or absence of conduction electrons and the size of the forbidden energy region, also called the band gap. If there are electrons in the conduction band at zero kelvin, the material is a conductor. Materials with an empty conduction band and a large band gap are insulators, while those with a small band gap are semiconductors. The difference between semiconductors and insulators is one of degree, the band gap for a semiconductor is small enough to allow thermally excited electrons to jump to the conduction band. Thus, semiconductors become better conductors as temperature increases. The thermally excited electrons in the conduction band provide a means for current flow, as does movement of the newly formed holes in the valance band. The electrons can also be excited by an applied voltage or from incident photons with energies equal to, or greater than the band gap energy. (1)

2.1.2 Intrinsic and Extrinsic Semiconductors Semiconductors which have conduction electrons and holes caused solely by thermal excitation are called intrinsic semiconductors. Silicon is a good example with a band gap of 1.2 eV, small enough to allow electrons at room temperature to move to the conduction band. Another way to put electrons in the conduction band, or holes in the valance band, is to add impurities to the crystal. If the same silicon semiconductor, which is a group IV element on the periodic chart, is mixed with a small amount of a group V impurity, the impurity will substitutionally replace a silicon atom in the lattice and bond to its neighbors. The group V elements have five valence electrons and only four are needed to bond to the crystal, the fifth is weakly held and will break free, becoming a free electron without leaving a corresponding hole in the valance band. This is an extrinsic N-type semiconductor.

If the silicon had been doped with a group III impurity, the resulting extrinsic semiconductor would be P-type. The group III elements only have three valance electrons and would be missing one to complete the crystal bonding. This leaves more holes in the crystal than conduction electrons.

2.1.3 Rare Earth Elements in GaAs This experiment uses a III-V semiconductor, GaAs. The rare earth elements are implanted into the GaAs substrate crystal. The process of implantation damages the crystal structure causing dislocations and point defects. To repair the damage the sample is annealed. The annealing process heats the semiconductor from 680° C to 725° C for about ten to fifteen minutes to allow the crystal to reorder itself and set the impurity into the proper sites.(2) The duration and temperature for the annealing process is determined by the type of substrate and impurity.

The rare earth impurities are normally in a trivalent state in a crystal such as GaAs. As such they replace the IIIb Ga. The rare earths form a NaCl structure, as compared to a zinc blende structure for GaAs. The resulting solubility of rare earths

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is poor, because a simple amalgamation of the two structures can not be expected.(3)

2.2 Transitions

The rare earth emissions are caused by transitions within the partially filled $4f$ shell. The energy levels which produce these transitions in the $4f$ shell are caused by spin orbit splitting. Normally, the energy levels within a shell will be split predominately by the material's crystal field, with the spin orbit causing a further splitting of smaller magnitude. However, the rare earth elements have filled $5s$ and $5p$ shells that screen the inner $4f$ electrons from the crystal field. The result is that the spin orbit coupling is the major factor determining the energy levels of the rare earth ions in a crystal. The crystal filed splitting is small relative to the spin orbit splitting. Figure 1 shows the spin orbit energy levels for the rare earth elements. and the transitions that are being studied. (4)
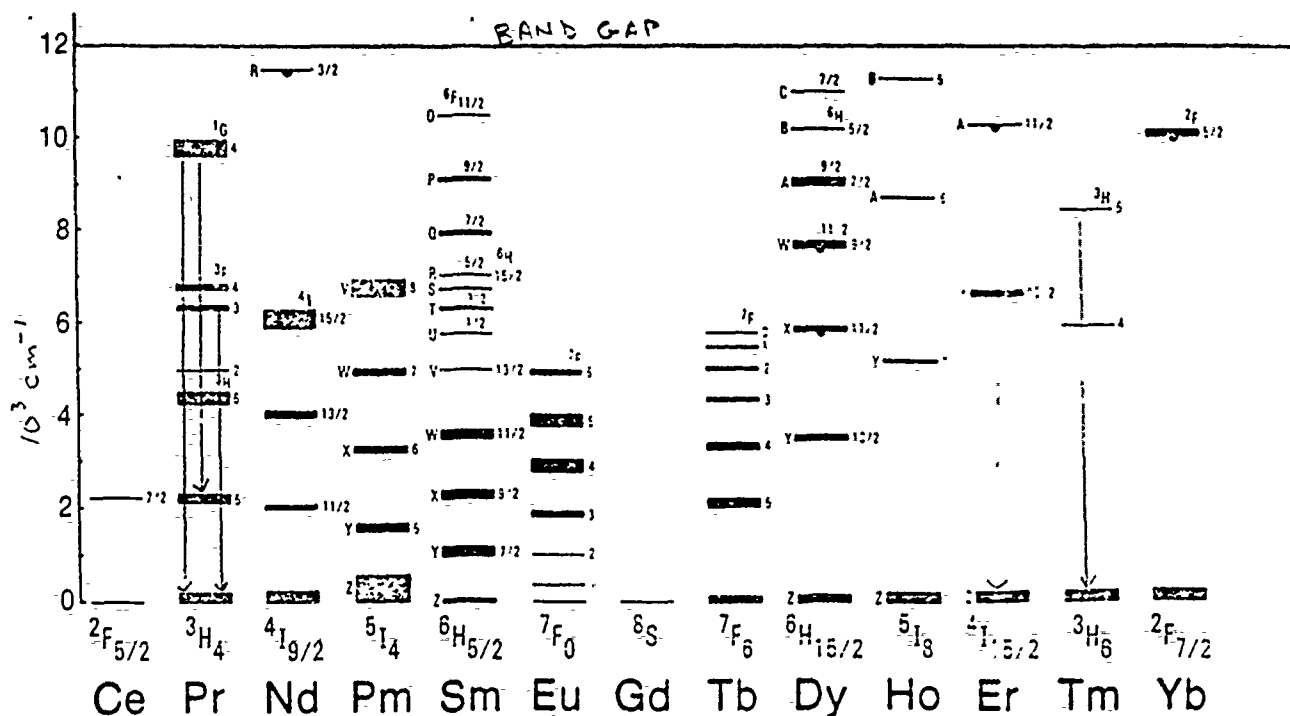

Figure 1. Energy levels of triply ionized rare earths in $LaCl_3$.
(4)

Figure 2 shows the relative magnitude of the crystal and spin orbit splitting.

The number of levels associated with the crystal field splitting is for illustrative purposes only. The number of levels and the spectral peaks for Er, Pr or Tm have not been completed at this time. Figure 3 shows an example of a rare earth ion, Yb, which has had the crystal field levels mapped out. (5)
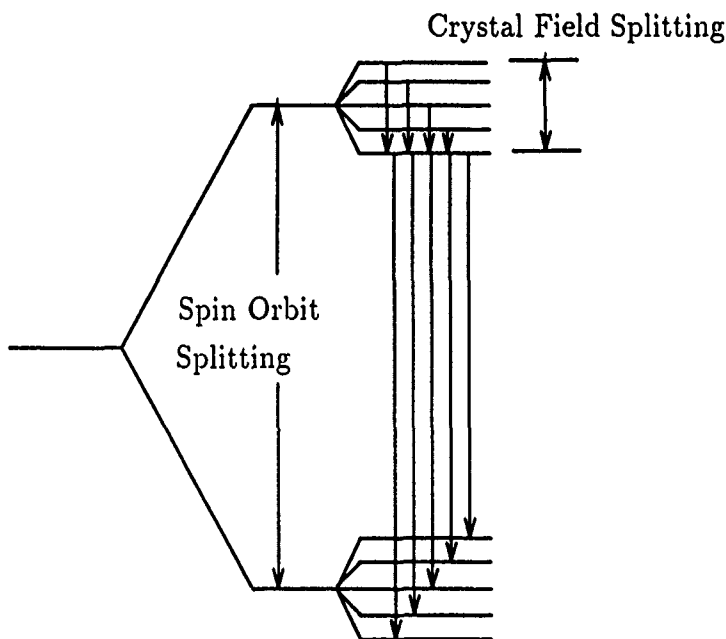
Figure 2.   Relative magnitude of crystal field and spin orbit splitting for rare earth ions in a crystal.

The energy for the rare earth emissions are transferred to the impurity center by various mechanisms, rather than directly from the laser excitation source. There are many energy transitions taking place in the semiconductor which could be transferring energy to the rare earth centers. There is the possibility that the rare earth ion could absorb a photon produced by the transition, but the dominant energy transfer mechanism occurs when the rare earth ion is directly involved with the transition. Figure 4 shows the various transitions possible.

Band to band transitions occur when an electron drops from the conduction band to the valance band. A photon is emitted with the energy of the band gap. The rare earth ion can not take part in this process, so the energy transfer is radiative.

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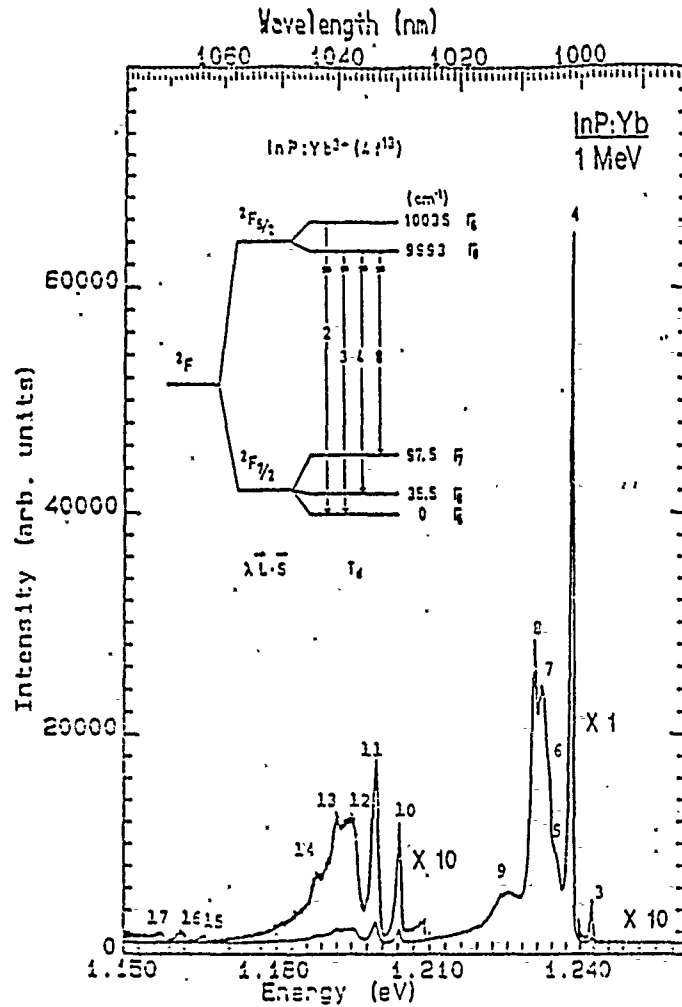
Figure 3. Spectral intensity of crystal field levels in Yb.

(5)

Free-to-bound transitions are either acceptor free-to-bound or donor free-to-bound. The process is again radiative with the energy of the emitted photon smaller than the band gap by the amount of the ionization energy of the dopant. The emitted energy from acceptor free-to-bound transitions can be transferred directly to the $4f$ shell of the rare earths.

Donor-acceptor pair transitions can occur in materials with both donors and acceptors, like GaAs. The hole on the acceptor and the electron on the donor are attracted to each other and the net energy emitted is the band gap energy minus the binding energy of the donor-acceptor pair.

Excitons are pairs of holes and electrons which orbit one another in the crystal, either bound to an impurity or freely moving. The ionization energy of the exciton is very low and can only be observed at low temperatures. The energy of a photon produced by a free exciton is less than the band gap by the binding energy. The photon energy from a bound exciton is even less than that of the free exciton by the energy required to bind the exciton to the impurity.

1: BAND TO BAND	Eg=Energy Gap
2: ACCEPTOR FREE-TO-BOUND	Ed=Donor Energy
3: DONOR FREE-TO-BOUND	Ea=Acceptor Energy
4: DONOR-ACCEPTOR PAIR	Ex=Exciton Energy
5: FREE EXCITON	Ec=DA Coulomb Binding Energy
6: BOUND EXCITON	Eb=Exciton Binding Energy
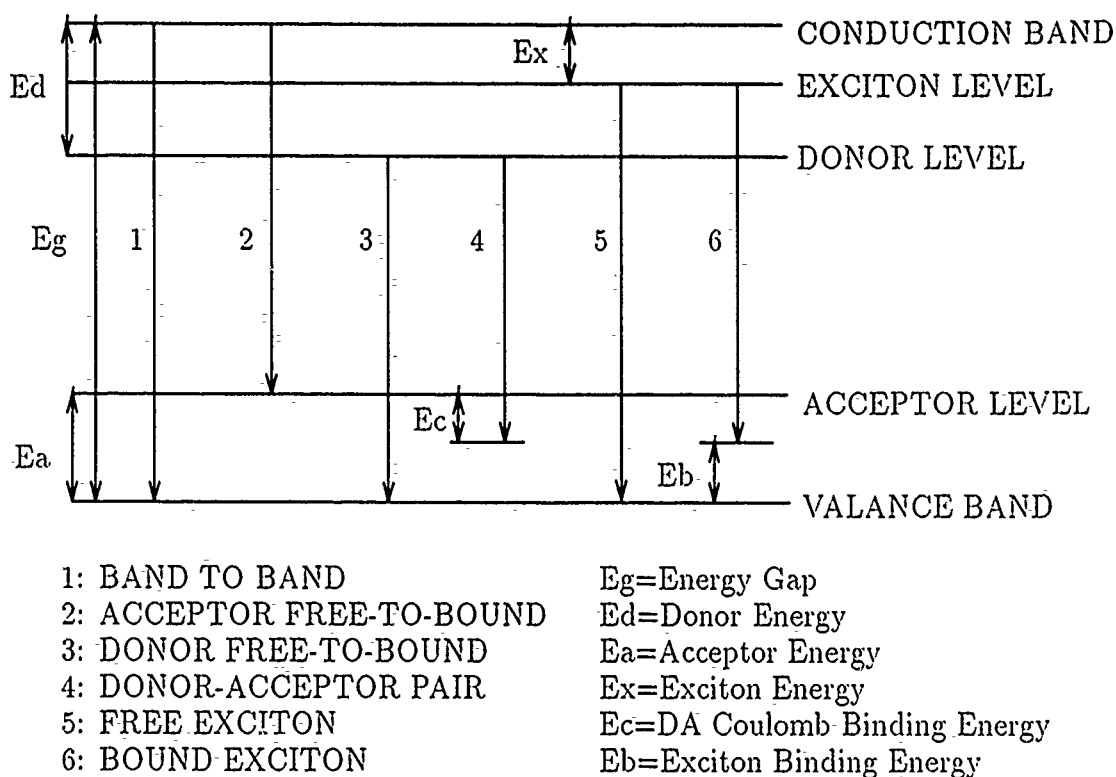
Figure 4. Various transitions in a semiconductor.

(6)

2.3 Photoluminescence

Photoluminescence (PL) produces an emission spectrum for the semiconductor. Normally, the semiconductor is illuminated with a continuous laser beam with enough energy to excite the transitions. The emissions are directed to a high gain detector through a scanning monochromator. As the monochromator moves through the spectrum the output changes as a function of the emission strength. The scan

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rate is relatively slow to provide good resolution, because normally the detector response is slow. All of the samples used for this experiment have had a PL spectrum run as part of another study and is shown in the results section.

Prior to taking data, there was some concern that the measurements might be in error if it couldn't be shown that the proper emission peak was used for the decay measurement. The solution was to perform PL on the samples using the same set up that would be used to measure the fluorescent lifetimes. There are significant differences between the type of equipment used for the two measurements, i.e., lifetime measurements need a pulsed laser and a fast response detector.

To acquire PL data with a pulsed laser, a boxcar signal averager was employed to gather the pulses and output a signal that the oscilloscope could use to display the spectrum. The boxcar sequentially samples time slices of an input signal. Each time slice is sampled a large number of times, and then the boxcar move to the next time slice of the input signal. The final values for each slice are output at a rate that can then be displayed on an oscilloscope, producing a representation of the original wave on a much longer time scale.

The PL spectrum shows the total emission for each wavelength regardless of the decay time. In a regular PL setup the signal strength at a given wavelength is an integration of all the radiation at that point for at least a second. The boxcar is limited to short integration times, less than a few tens of μsec. The spectra obtained from the pulsed system is different than those of obtained with a continuous laser system, because of the difference in integration time. The boxcar can only output the decay signal level for a small segment of the decay curve, fortunately the segment can be moved along the decay curve. With the system here the relative size of the segment and its position can be adjusted to provide PL spectra for various time slices after the laser pulse, this kind of sampling is called Time Resolve PhotoLuminescence (TRPL).

2.4 Fluorescent Lifetime Measurements

A fluorescent lifetime measurement determines the decay rate for radiation from a particular transition. In applying this method the first step is to excite the valence electrons with enough energy to cross the band gap. In this case a laser is used with a very short pulse, a few nanoseconds, to prevent it from interfering with the decay signal. The electrons begin to lose energy and fall back to the valance band emitting photons via the appropriate transitions. Those transitions associated with the rare earth elements transfer their energy to the partially filled $4f$ shells, thus producing the characteristic rare earth line emissions.

A semiconductor will have a number of different characteristic emission lines, each having a finite bandwidth. The rare earth emission is isolated using a monochromator set to the wavelength of the line. For the highest possible resolution the slit settings on the monochromator must be as small as possible, yet large enough to prevent significant signal loss. Furthermore, if the monochromator passes too large a bandwidth the decay rate will be a mix of the decay rates of the intended signal and the emissions on either side of it, thus introducing error into the measurement. For all measurements made for this experiment the slit was set at 2 mm, providing a resolution of 3.3 nm.

The monochromator directs the light to a detector which converts the signal to a proportional voltage and amplifies it. The detector must have sufficient gain to pick up weak signals and also have a response time fast enough to resolve short decay times. As with most things in life these two factors are mutually exclusive and have to be traded off against one another. That is, a fast detector response time reduces the amplification. Fortunately, a fast response time was achieved with sufficient gain to allow observation of the rare earth emissions.

The decay rate of the electrons falling in a given transition is usually exponential, and could possibly show a double exponential decay. The exponential signal will be mixed with random background and electronic noise. To reduce noise the

emission is sampled a thousand times. As each curve is sampled, it is averaged, point by point, with the previous decay curves. The final decay curve is a cleaner representation of the real decay, because the random noise will tend to average to zero and the signal will tend toward its average value. The raw signals are averaged using a digital oscilloscope. The oscilloscope is triggered by the laser to ensure the data acquisition is started at precisely the same point in time for every decay curve. The final signal is then analyzed and fitted to an exponential curve. The decay lifetime is the time for the signal strength to fall to $1/e$ of the original value.

2.5 Previous Work

The original idea for a rare earth doped semiconductor laser was proposed by R. L. Bell in 1962 (7). He outlined a DC pumped laser where radiative emissions from the band gap are absorbed by the inner $4f$ shell of a rare earth impurity center. The excited $4f$ levels would then relax through a number of transitions. The goal would be to produce enough excited impurity centers to allow lasing of the system.

Also in 1962 Ofelt, and Judd separately looked into determining the intensities of the $4f$ rare earth emissions. The results of the two studies were to explain some of the observations already made with rare earth materials like $PrCl_2$ and $EuCl_2$. Despite the partial success it was also concluded that further research was needed. (8, 9)

More recently research has moved to InP:Yb. The decay of InP:Yb has been measured a number of times, including the two previous masters students and a PhD student here at AFIT. The Yb emission in InP is relatively strong compared to the Er, Pr and Tm in GaAs currently being looked at. The Yb emission was also measured during this effort as a system check. The decay time was determined to be 11.5 μseconds. The work done with Yb may be used for other rare earth studies. The decay life time was measured as a function of annealing temperature and time. The decay time tended to increase with increased annealing temperature

and decrease with increased annealing time. In this case the samples were prepared by ion implantation and other methods of doping may show different trends. (10)

In his PhD dissertation published in December 1989, Pomrenke, attempted to measure the decay times of Er, Pr and Tm. The decay times he observed were so close to the system response time that the results were inconclusive. (2) In an article, dated 21 October 1988, Klein and Pomrenke reported a successful measurement of the 1.54 μm Er decay in Si, InP, GaP, and GaAs. The samples were doped in various ways, but the decay times were all about 1 millisecond.(11) Benyattou et. al. also measured the decay lifetime of Er at 1.54 μm, but in AlGaAs. They report a double exponential decay with 260 μseconds and 1.17 milliseconds for samples prepared using molecular beam epitaxy. (12) There have been no reports on the measurements of the decay times of Tm or Pr. This is the first published decay times for these rare earth elements, to the best of my knowledge.

III. Experimental Setup and Operation

The equipment configuration used to measure the rare earth fluorescent lifetimes is shown in Figure 5. Additionally, a personal computer is used for data storage and processing. Previously, this equipment was used in support of two Masters theses. In addition to measuring Yb decay lifetimes the first student built the basic set up and the second improved it and moved it to the present location. During the last 3 months more changes have been made to increase the capabilities of the laboratory. The equipment described here is from the final configuration.
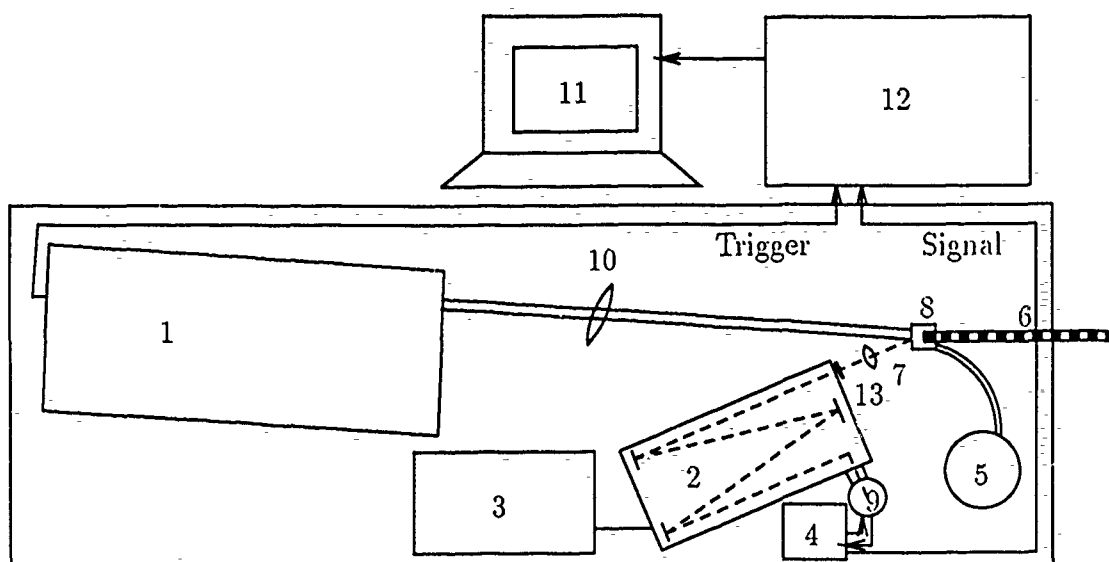
1 Nitrogen Laser
2 Monochromator
3 Monochromator control
4 Power for detector and Pre-amp
5 Turbo-molecular pump
6 Helitran
7 lens
8 Vacuum sheath
9 Detector

10 Fused silica lens
11 Equipment rack
    Digital O-scope
    Boxcar averager
    TMP Control
    Temperature control
    Pressure gauge control
12 Computer
13 0.83 micron long pass filter

Figure 5. Experimental set up

3.1 Excitation Source

The first step in measuring decay lifetimes is to excite the electrons in the semiconductor. A LaserPhotonics Model UV-24 nitrogen laser is used here. This laser was originally used to pump a LaserPhotonics Model 14 dye laser. The beam is shaped like a rectangle with a height of 1 cm by 2.5 cm. The nitrogen laser output power is rated at 330 milliwatts of ultraviolet laser light. This system is desirable for two reasons, pulse length and high power out. The pulse width of ten nanoseconds is very short compared to the expected decay times in the millisecond or microsecond range. The laser has a synchronization signal output that is used for all the timing during the experiment.

3.2 Wavelength Selection and Signal Detection

The SPEX 500M spectrometer (monochromator) is used to select the wavelength of the emission. This 0.5 meter focal length monochromator with f/4 aperture was a late addition to the experiment. Both the input and output slits are variable from 2 μm to 2000 μm, and a best resolution of 0.02 nm. The linear dispersion in the first order is 1.6 nm/mm for the 600 gr/mm grating. The grating has a blaze of 1.6 μm, which provides sufficient spectral range for the wavelengths to be studied. The wavelength can be set remotely to a given value or the monochromator can be put into a scanning mode to look at a range of wavelengths. The rate of scan is variable to accommodate the resolution needed.

The light from the monochromator is directed to the detector via a curved mirror in a sealed housing which connects to the monochromator output mount and the bottom of the detector. The mirror can be adjusted to direct the light to the active detecting area on the bottom of the detector.

The fluorescence decay is measured with a North Coast model EO-817P Germanium detector having a 300 - 400 nanosecond response time. The spectral response is 0.8 to 1.7 μm. It is a liquid nitrogen cooled detector with an active detector area

of 25 mm^2. It uses -450 volt bias and ± 12 volts for the electronics. The voltages were supplied by two separate power supplies.

Because the emissions from the rare earth elements are very weak, an EG&G model 115 wide band preamplifier is used to increase the signal coming from the detector to the oscilloscope. It provided a voltage gain of 10 or 100. The preamplifier has a frequency response between DC and 70 MHz and a rise time of 7 to 7.5 nanoseconds. The power requirements are ± 12 volts and are supplied by the same low voltage power supply used by the detector.

3.3 Boxcar Averager for Spectral Information

The weak emissions call for special measures to be taken to ensure the correct emission line is sampled. An EG&G model 162 boxcar averager with a model 165 gated amplifier is used to facilitate the collection of a PL spectrum. The monochromator is set to scan the spectrum at a known rate and the boxcar is set to sample the emissions. The output is a voltage level that will change as the monochromator scans through the spectrum. The system is triggered directly from the nitrogen laser.

3.4 Data Collection and Reduction

Data collection and display is performed by the same instrument, a LeCroy 9400A Dual 175 MHz digital oscilloscope. The oscilloscope has features such as signal averaging and data storage which make the task of data acquisition straight forward and quick. It has a slow scan setting that is used for obtaining the photoluminescent spectrum. The time interval can be set as high as one hundred seconds per division. Another important feature is signal averaging, i.e. the scope display can be averaged over as many as ten thousand times. The final averaged waveform is displayed on the screen and can be temporarily stored in one of two memories until later retrieval by the computer. The scope generates a maximum of 25,000 values per waveform, this large number of data points allows for a high degree of accuracy later during

curve fitting. The digitized data can be transmitted via an RS-232C cable from the either of the two memories to any IBM PC compatible computer.

A Z-248 personal computer is used for data processing and permanent storage. The LeCroy manual provides a simple Basic program that will interface the LeCroy oscilloscope to any IBM compatible personal computer through its RS-232C port. The program sets up the RS-232C port so that it can transmit commands and data at a rate of 19200 baud to and from the oscilloscope. The set up allows communications both ways and data can be transmitted to the oscilloscope if the need arises. The program outputs the data in ASCI II form and writes it a file specified by the operator.

Even though the data file is in ASCI II, it is not in a form usable by curve fitting or plotting programs. Another basic program was written to convert the files to a usable format. The format was: x-value y-value, with no commas or semicolons between the values. This format is readable by Gnuplot for graphic display and insertion into the text of this thesis. The program scales both axes with the time scale and voltage used during data acquisition.

Once the data is in the computer it has to be reduced to determine the lifetime of the decay. The fluorescent decays are exponential, so an exponential curve fit is performed. A nonlinear least squares curve fitting program was written that runs on the Z-248 and takes data in the format used by the conversions program.

It was easier to write another program that would perform a least squares fit of the data to the function $Y = e^{-AX+B} + C$ than use something like Mathmatica. The background term, C, is found by averaging the last twenty five data points in the file. Other programs couldn't handle the data because they performed a linear least squares fit to the natural log of the data. This would cause problems when a data value was zero or negative. The program is not fast, so to save time it is set up to process any number of data files sequentially. The outputs, all the dependent variables are written to a file. The fluorescent lifetime is then, $\tau = 1/A$.

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The final piece of software was a plotting routine that plots the data on the computer screen. The program is needed to confirm that the data is indeed what was measured. It will plot up to four sets of data at a time.

All of these programs work well with each other and the output provides data in a usable format, but it would be more convenient if they were combined into an integrated package to acquire and reduce the data for this laboratory. This should be considered for any follow on experiments.

3.5 Cooling and Vacuum Systems

The samples need to be cooled during the measurement for the decay to be detectable. The cooling system used in this study is able to cool the sample down as low as 4.5 K and or to any specified level. The Air Products Helitran and Digital Temperature Indicator/Controller perform this task nicely.

The Helitran transports very cold helium gas from a helium dewar to the cold finger holding the sample. The Helitran transfer tube is a triple jacketed helium transport hose with a central flow of helium that goes from the helium dewar to the cold finger. At the cold finger the gas is exhausted to the room. Surrounding the central tube is a second flow in a wider tube that is concentric to the central one. The second flow isn't exhausted when it reaches the cold finger end of the Helitran, instead it is pulled back through the third layer of the Helitran and is exhausted at the transfer tube end. Both the central and outer flows are controlled by needle valves. This design significantly reduces radiative losses from the central flow and allows the system to bring the temperature to 4.5 K in a matter of 30 minutes.

The cold finger is a copper mount measuring $1 \times 2 \times 4$ cm, and is secured to the end of the Helitran. An Indium washer is placed between the cold finger and the Helitran to ensure a good thermal contact. When the cold finger is mounted on the Helitran it is situated inside a cylindrical copper casing that acts as a heat shield. The heat shield has two rectangular openings to allow the laser beam and return

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signal to pass through it. The shield is there to reduce the radiative heating of the cold finger.

The Air Products Digital Temperature Indicator/Controller displays the temperature of the cold finger and samples. It uses heaters that can raise and hold the temperature of the samples at a specified level. The temperature is set by dialing it on the front panel, and selecting the heater power. The maximum power to the heater is 12 watts. To minimize He use the central and outer needle flow valves can be adjusted to reduce the cooling of the cold finger.

The samples are in a vacuum during the decay measurements. The end of the Helitran attaches to a vacuum sheath that encases the sample, cold finger and heat shield. The vacuum system consists of an Air Products vacuum sheath, a mechanical rough pump, and a Leybold-Heraeus Turbo Molecular Pump (TMP). The TMP is controlled by a Leybold-Heraeus Turbotronics NT220 controller mounted on the equipment rack near the optical bench. The vacuum system can pump the system down to the required pressure, 10^{-6} torr, in about twenty minutes.

3.6 Optical Elements

Various optical elements were needed to direct the laser to the sample and then direct the decay signal to the monochromator. These included a UV filter and two lenses. The first lens is made of fused silica and is used to focus the UV laser beam on to the target sample. This lens is turned with respect to the beam to produce an astigmatic image of the laser beam on the target to get more power from the rectangular beam on the sample. An 830 μm long pass filter is used to stop stray UV and second order emissions from entering the slit of the monochromator. The second lens is used to focus and direct the decay signal to the entrance slit of the monochromator.

3.7 Significant Changes to the Laboratory

This laboratory has been used twice before to measure the decay of rare earth elements. (10, 13) The lab set up and equipment used this time has changed in a number of important ways from the previous experiments. Previously the decay data was collected with the boxcar averager, which would average only one point in the entire decay curve a given number of times. The number of times the data was averaged was dependent on the sampling window and the number of segments in the window. At its best the boxcar was sampling between twenty to fifty point for every data point output. The LeCroy can average up to 100,000 wave forms if the need arises. The output of the boxcar was then input into a software package called Asystant Plus which could then average a number of complete scans from the boxcar. The number of scans averaged together was normally only twenty. The software was cumbersome and the data acquisition time was a lot longer than that required by the LeCroy. Additionally, the LeCroy is basically a digital storage oscilloscope, so the old analog oscilloscope was no longer needed. The LeCroy replaced two pieces of equipment and improved the experimental set up immeasurably.

In previous experiments the signals were strong enough that a photoluminescent spectrum was not needed to ensure the emission was the proper one. The boxcar averager is still used, but only to sample a segment of the decay and output a voltage to the oscilloscope. With the oscilloscope on 20 seconds per division, this provides a PL spectrum.

The high power of the nitrogen laser provided stronger emissions from the samples. The previous experiments used the dye laser with its rated efficiency of 15%. Prior to this experiment, the maximum power to the sample was 9 milliwatts. Without the dye laser, power to the sample has increased greatly to a maximum power of 330 mW. However, the signal to the LeCroy is still weak and the new preamplifier is needed to boost the signal strength to an adequate level for acquisition.

The vacuum sheath and heat shield have two openings at 90 degrees to each

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other. This allows the beam to enter one opening and the signal to exit through the other. The system was reconfigured so both the signal and laser pass through the same opening. The signal strength wasn't increased noticeably, but the background noise level was greatly reduced.

The significant difference in this experiment from previous ones is that decay of some very weak emissions were able to be measured. All of the changes discussed above contributed to my success. The net effect of these changes is an increased power to the sample, improvement in the signal to noise ratio, a stronger decay signal to the data acquisition and storage equipment, and provide a much shorter data acquisition time while sampling more wave forms.

3.8 Procedure

The start up of the laboratory takes about an hour from complete shut down to signal out. The order of start up of the equipment is largely arbitrary, the only consideration was the time needed to allow certain pieces of equipment to cool and others to warm up electronically.

First, turn on the boxcar averager which takes 30 minutes to warm up. After the warm up a short 5 minute calibration is performed. The Ge detector has to be cooled to liquid nitrogen temperatures before power can be applied. Filling the detector with liquid nitrogen takes about 10 minutes and then it should be left to cool for one half hour before power is applied.

Next, two samples are mounted on the cold finger. Crycon vacuum grease is applied to the back of the samples and then each is carefully pressed on to the cold finger. The samples are then positioned so that the surface of the samples are as close to parallel to the surface of the cold finger as possible. The cold finger is then attached to the Helitran and positioned to face the opening in the monochromator. The heat shield is then placed around the cold finger, ensuring one of the openings is positioned to allow the laser and decay signal to enter and exit unobstructed. The

vacuum sheath is then put in place, and aligned properly. The system is pumped down using the rough pump. Once the system pressure is below 10^{-1} torr the TMP is switched on, and the pressure drops to the 10^{-6} torr range in about 15 minutes.

The samples may be cooled as soon as the vacuum is down to 10^{-6} torr. The bayonet end of the Helitran is lowered into the helium dewar and the flow valves opened fully. The needle flow valves are adjusted periodically and a shroud heater started while the system cools down to the temperature needed. The heater is not the sample heater, but is used to prevent ice build up on the outside of the helitran in and around its fittings.

While the detector and cold finger are cooling, the nitrogen laser can be started along with its pump. The nitrogen laser takes 15 minutes warm up. After the 15 minutes the delay light will go out and flow of nitrogen started by opening the valve and setting the pressure to about 50 torr in the laser cavity. The start button is pressed until the laser starts, normally 10 to 15 seconds.

Once everything has had enough time to become operational, the final pieces of equipment to turn on are the pre-amplifier, the oscilloscope, the computer and the detector. One then needs to ensure the temperature of the cold finger is at the desired level, put the laser beam on one of the samples, and make a few course adjustments to the lenses to get the signal into the detector. The monochromator is set to the wavelength of the GaAs band gap emission. This emission is very strong and as such it is easily found. With the band gap emission decay displayed on the oscilloscope the optics are adjusted for the best signal strength. This step ensures the signal about to be measured is originating from the sample and the optics are positioned for maximum signal into the detector.

The boxcar and the oscilloscope are set for measuring the spectrum. The oscilloscope is set for 10 seconds per division giving a 100 second full screen trace. The boxcar is set to sample the emission and output a voltage proportional to its strength. Finally, the monochromator is set for a 100 second scan of the spectrum

where the decay is expected. The spectral scan is saved and the monochromator is set to the wavelength corresponding to the rare earth peaks in the spectrum.

Five decay curves are obtained for each sample. The decays are averaged to determine the decay value and the standard deviation used as the error. The response time of the detection and acquisition instruments is a limiting factor on the decay time that can be measured. The final decay value is then:

$$\tau^2_{final} = \tau^2_{measured} - \tau^2_{systemresponse}$$

After both samples are finished, the system temperature is raised to 293 K, and the samples changed. To raise the temperature, the bayonet is raised out of the liquid helium in the dewar, and the needle flow valves are shut. During the change the rest of the equipment is left running, except the laser. At the end of the day the temperature is raised, and all the equipment shut off, with the nitrogen laser being the first to be shut down to conserve the nitrogen. The samples are changed in about 20 minutes and the system pumped down in preparation for the next days measurements.

The files are converted and the curve fitting program is set to run over night, the reduced data will be stored on the computer and available the next morning. All of the raw data collected during the various runs is saved on the hard drive of the computer. The raw data files are not altered in any way by the conversion process.

IV. Results and Discussion

The decay of all five emissions could not be obtained, because of minor problems which were encountered. Three of the rare earth emissions were measured and the results are shown in Table 1. The remaining emissions will be measured in later experiments, when new components can be added to the system.

Table 1. Decay Lifetimes for Pr, Er, and Tm

	Decay time	Material
Pr	40 ± 7 μsec	SI, Cominco, 750/10 m, fg
Er	360 ± 58 μsec	SI, CS467974, 5E13, 1 Mev, 680/10 m, fg
Tm	8.7 ± 0.8 μsec	SI, Cominco, 217598, 725/15 m, H_2

The Er emission is about a factor of three smaller than the lifetimes reported by Klein and Pomrenke, and Benyattou et. al. The signal was not good enough to reliably see a double exponential. Er emission was the weakest of the three and this could be the reason for the discrepancy in the decay times.

The important question concerning the decay lifetimes shown in the table is, 'Were the correct emissions sampled?' To answer this question the PL spectrum of each sample was obtained using the same equipment that was used to measure the decay lifetimes. The monochromator could then be set to the wavelength indicated by the PL and the correct emissions could be measured. To get the PL spectra, the boxcar sampled a part of the decay signal, see Figure 6. The boxcar could not integrate the entire decay signal, if it could the PL would have definitely looked like that taken previously from these samples, see Figures 7 to 9. The boxcar was first set to sample the peak of the fast decay (0.34 μsec or less), Figures 10 and 11 show the resulting spectra. There is enough structure in these spectra to compare with the previous ones. Everything matches except the rare earth emissions are missing.
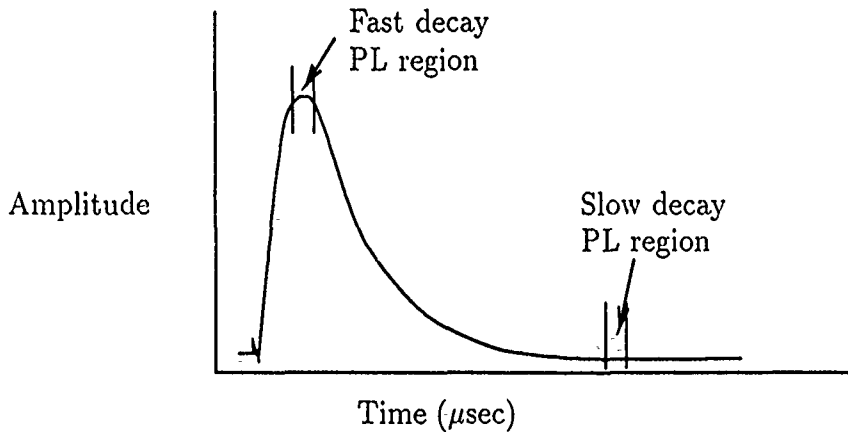
Figure 6.   Sections of the decay curve sampled for the fast decay and slow decay PL.

The Er PL showed nothing in the area corresponding to Figure 8. The rare earth emissions don't decay quickly, so the boxcar was set to sample at 12 μsec after the laser pulses. The results for all three samples were negative. The signals were too weak for this system to pick them out of the background noise.

The alternate method was to use the PL spectra provided by the earlier research to determine where to set the monochromator. The monochromator was calibrated to assure the correct wavelength was actually reaching the detector. Once the decay had been detected and recorded, the monochromator would then be set to a wavelength where there should be no emission above background. If the rare earth emission decay curve looked just like the background decay curve then the data was in doubt, but if the two were significantly different, then the decay was assured to be that associated with the rare earth impurity.

Figure 13 shows the Er emission at 1.54 μm and the background emission at 1.52 μm. The two emissions have been separated by adjusting the scaling after the data was collected. This figure clearly confirms the validity of the rare earth emission at 1.54 μm. Figure 12 shows the Pr emission at 1.38 μm and the background at 1.46 μm, again association with the rare earth emission is confirmed. The final rare earth emission decay is confirmed in Figure 14, where the Tm 1.232 μm line is shown

against the background at 1.208 μm.

The emissions were sampled one to five thousand times for the final output signal. The Er was sampled a thousand times, then the number was increased to two thousand for Tm to get better averaging, and finally set to five thousand for Pr. In future measurements the emissions should be sampled five thousand times, however, beyond this the acquisition time becomes restrictive.

Each emission line was measured five times and each output was fitted to an exponential decay. Figure 15 through 17 show the exponential fit against the actual data. The data is too noisy for any attempt to determine a double exponential decay. The decay times from the five were averaged to get the final decay value and the standard deviation was used as the error. The final value shown in the Table 1 has been determined using the formula in section 3.8.

The various runs for the final decay value were obtained by starting the sampling at different times after the trigger. The raw data for PM shows the decay time getting longer as the time after the trigger gets longer. At first, it was thought this showed evidence for a double exponential decay. It is actually caused by the digital nature of the oscilloscope and the low signal strength. All of the graphs show the data to be at discrete values. At very low signal strength in the tail of the decays, the output settles on one of the digital levels unable to represent the slow drop with accuracy. This can only be corrected by getting a stronger signal to minimized the digital effect.

The system response time was determined by measuring the near edge emission of all three samples and averaging. The near edge emission decay time is about 10 nanoseconds, so the decay measured is essentially the system decay time. The system decay time is 0.35 $\pm$ 0.01 μseconds.

Two of the Pr emissions were not measured. The 1.6 μm line is too close to the second order of the band gap. There was a 830 nm long pass filter at the entrance of

the monochromator, but enough of the band gap emission made it through to show up on the Pr PL spectrum. A 1 μm long pass filter is needed to completely filter the band gap and allow measurement of the 1.6 μm line. The other line, 1.1 μm was too weak. The peak on the PL was much lower than the 1.38 μm emission, so it was not even attempted with this set up.

The three decay curves were measured with the same monochromator settings, so that a comparisons of the signal strengths could be made. Figure 18 shows the strongest of each of the three samples, scaled properly for comparison.

The second goal of this experiment was to measure the fluorescent decay of the same rare earth emissions in semiconductors prepared differently i.e. different rare earth concentrations, different annealing temperatures, and different implantation energies. There was not enough time to perform these measurements, but the system has been proven and a follow-on experiment will not have the delays at the beginning that were encountered here.
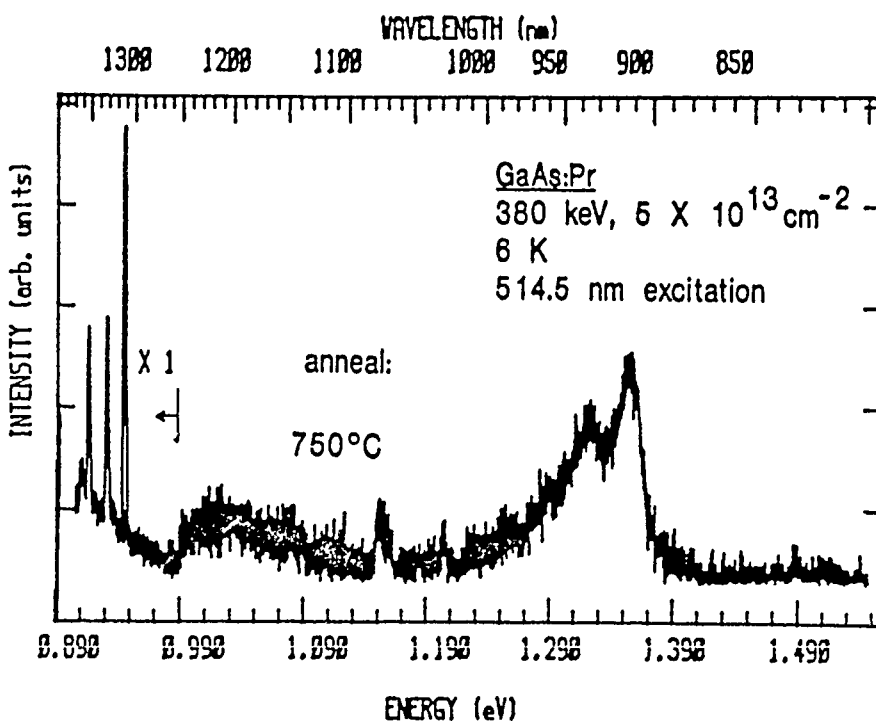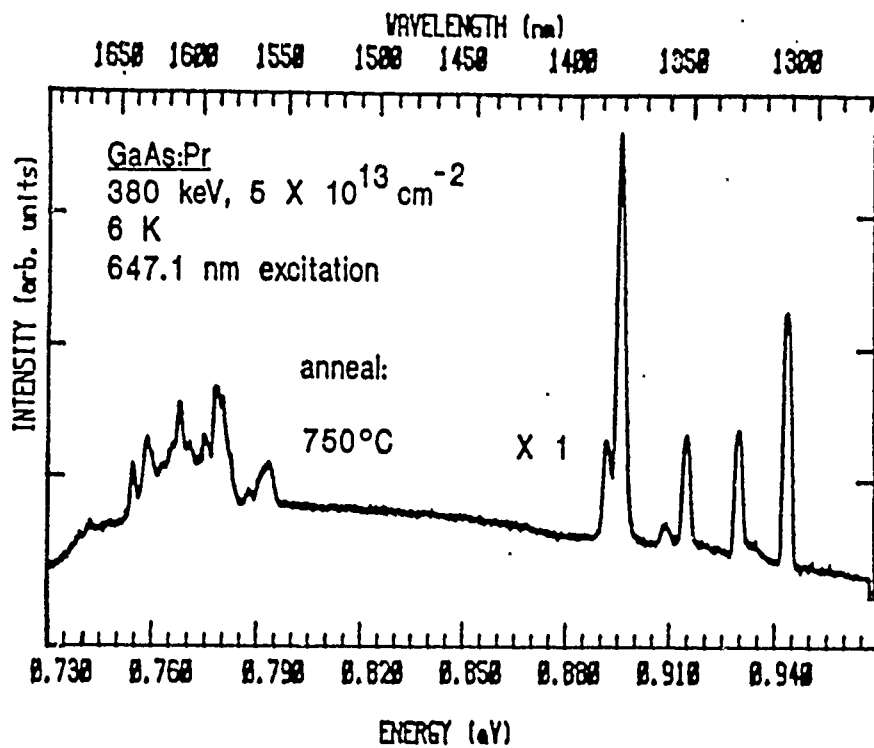
Figure 7. PL of Pr for the sample used in this experiment.
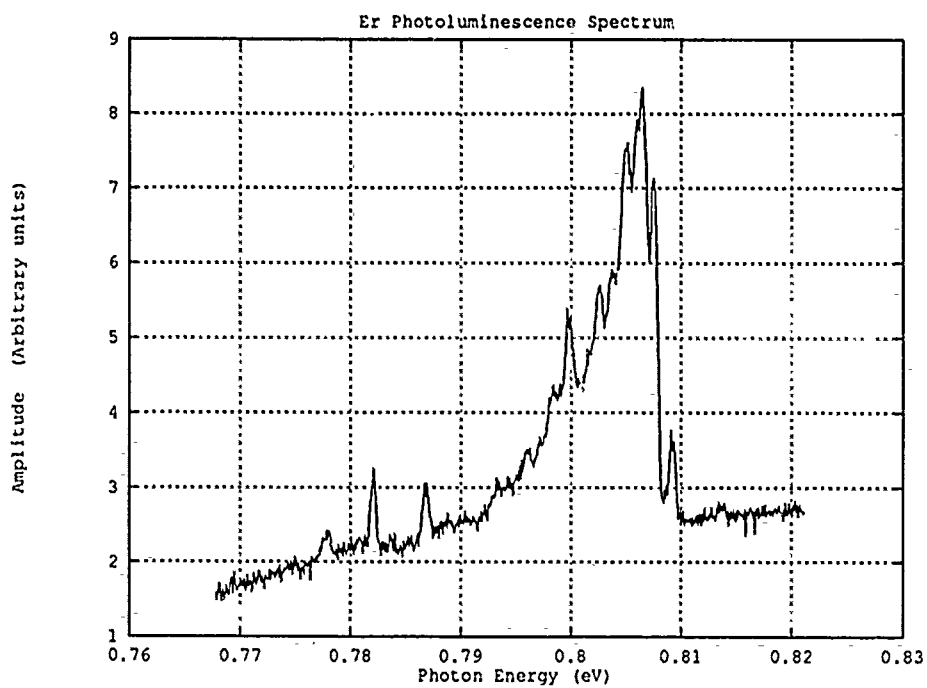
(2)

Er Photoluminescence Spectrum

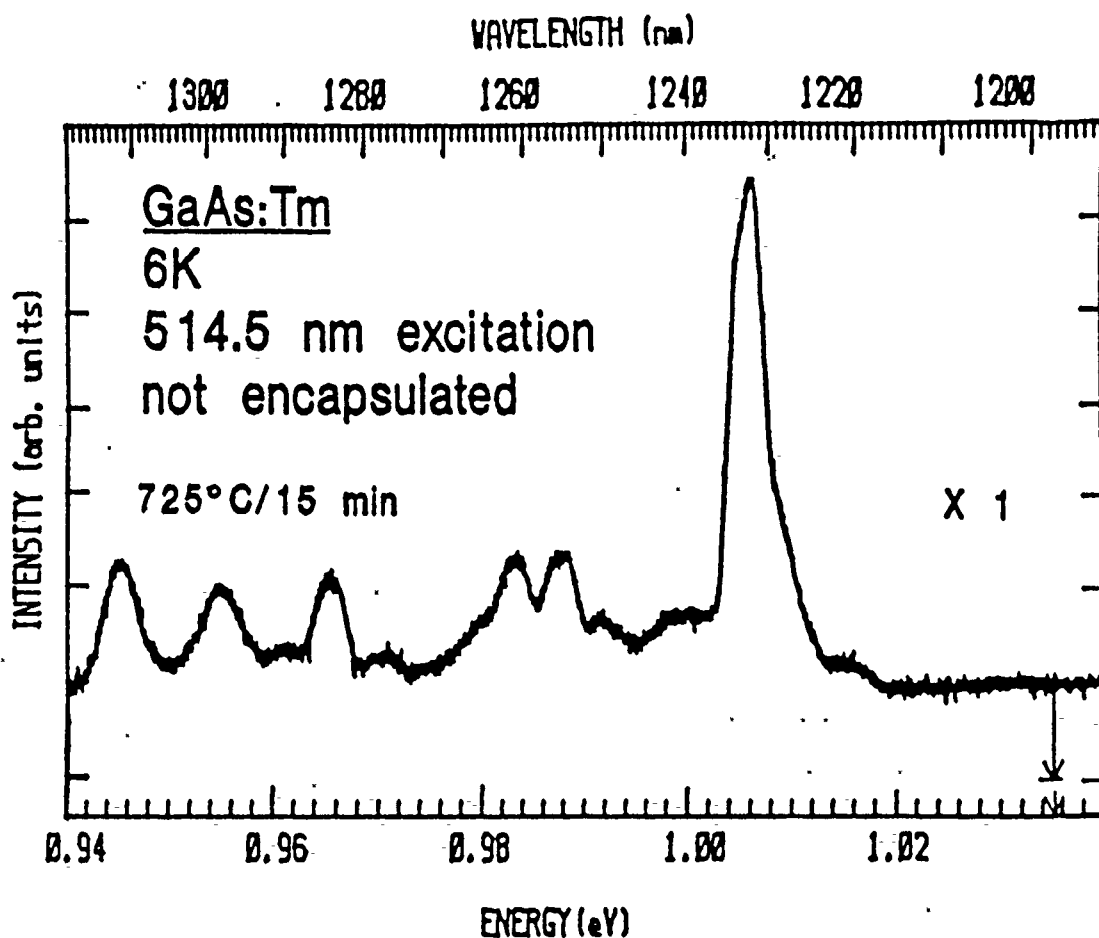Figure 8. PL of Er for the sample used in this experiment.

(5)

Figure 9. PL of Tm for the sample used in this experiment.
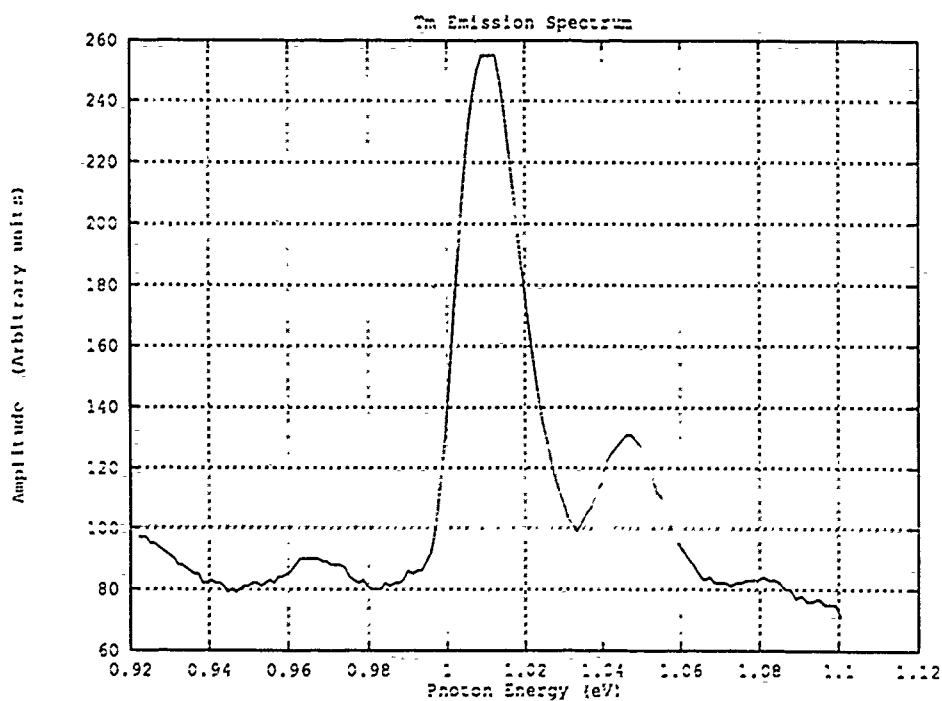
(2)

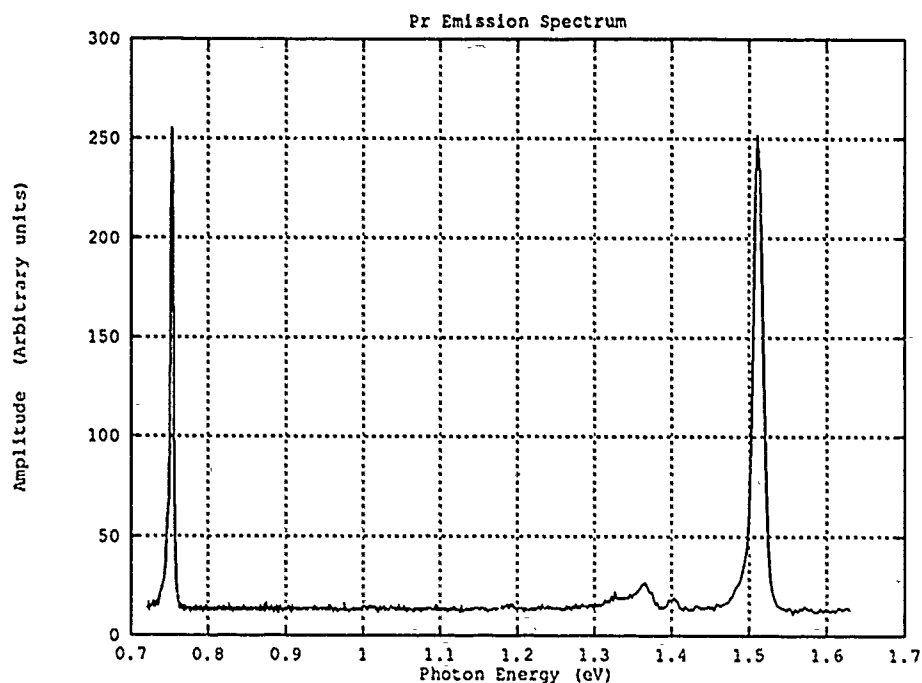Figure 10. Fluorescence decay spectrum of Tm in GaAs.

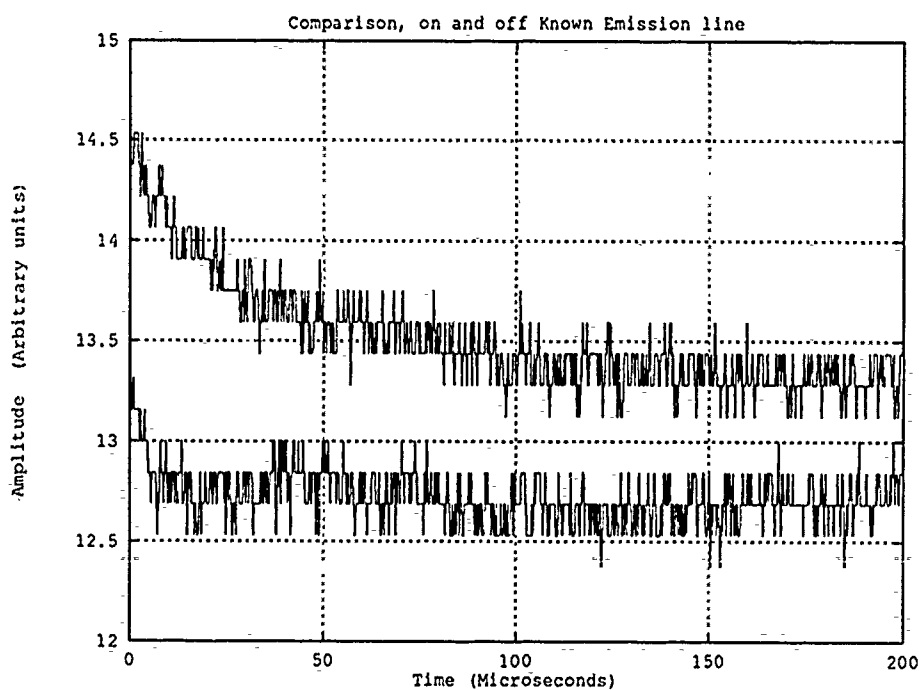Figure 11. Fluorescence decay spectrum of Pr in GaAs.

Figure 12. Fluorescence decay of Pr in GaAs at the expected position of 1.38 μm and the background at 1.46 μm.
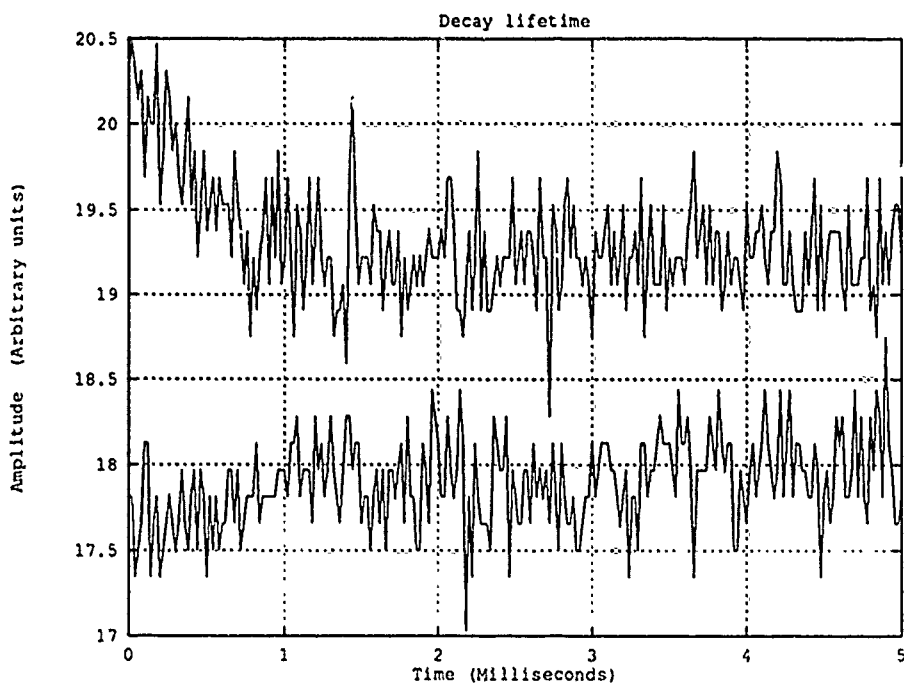
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Figure 13.   Fluorescence decay of Er in GaAs at the expected position of 1.54 μm and the background emission at 1.52 μm.
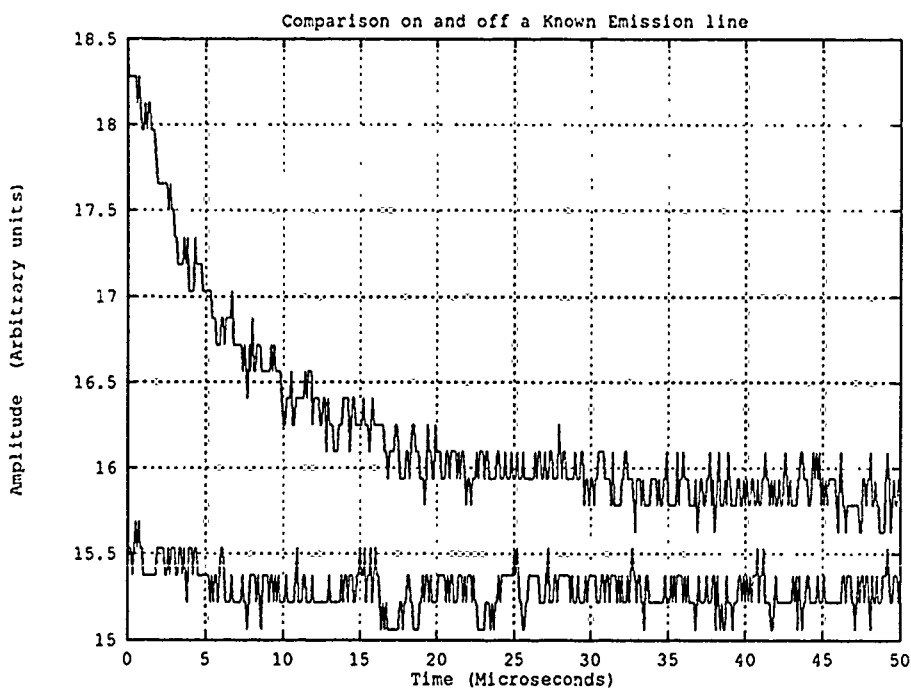

Figure 14.   Fluorescence decay of Tm in GaAs at the expected position of 1.232 μm line is shown against the background at 1.208 μm.
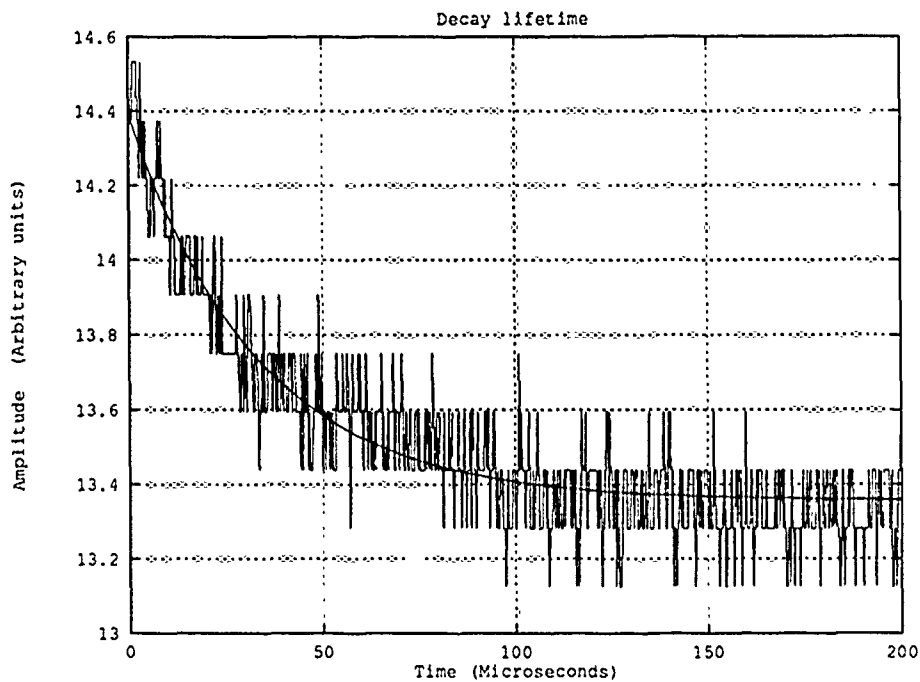
Figure 15. Fluorescence decay of Pr in GaAs and the curve fit. (Run 1)
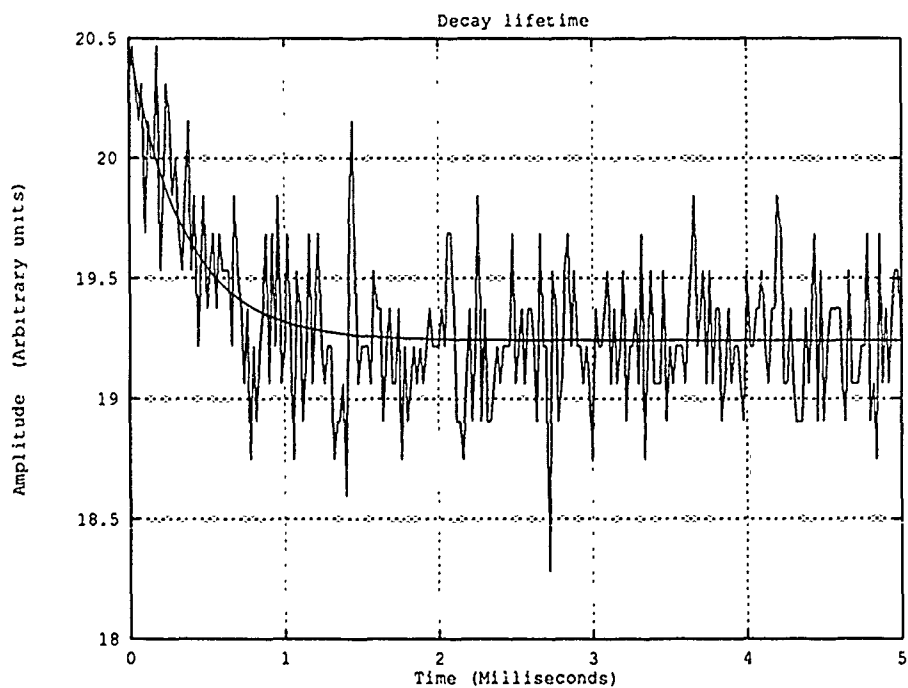

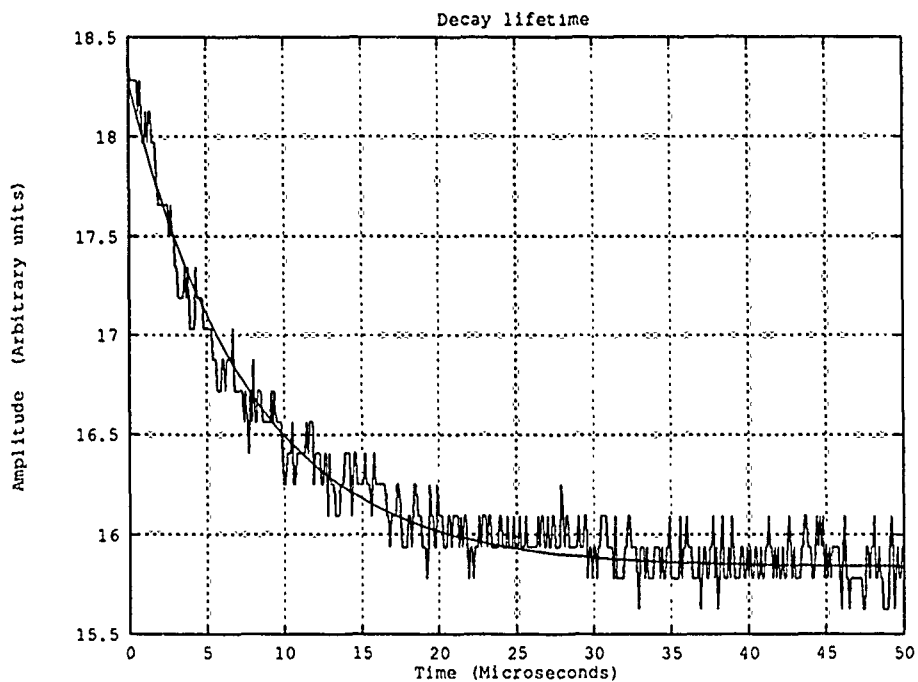Figure 16. Fluorescence decay of Er in GaAs and the curve fit. (Run 1)

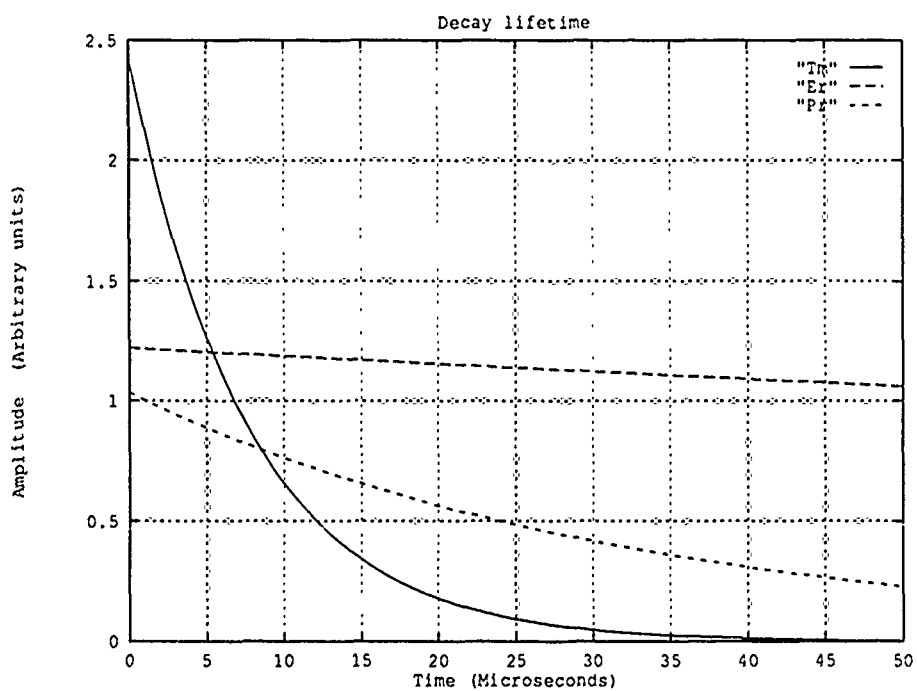Figure 17. Fluorescence decay of Tm in GaAs and the curve fit. (Run 1)

Figure 18. Fluorescence decay curve fits of Er, Pr and Tm in GaAs.

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V. Conclusions

This experiment succeeded in measuring for the first time the decay lifetime of the 1.38 μm Pr emission, the 1.2 μm Tm emission. The 1.54 μm Er decay lifetime did not agree with other reported lifetimes, but the measurement made here shows that for this particular sample the lifetime is long enough to be measured by a detector with a higher sensitivity and a longer response time. I have complete confidence in the Pr and Tm decay times, but the Er emission should be measured again with a more sensitive detector.

This experiment also shows the Tm emission to be the strongest and shortest of the tree lifetimes measured, and the Er to be the weakest and the longest. Further investigation is needed to see if this inverse relation between the lifetime and the emission strength is common for the rare earths.

The results of the Er reported here and by others are consistently between 260 μsec and 1 millisecond. In subsequent measurements of this Er fluorescent emission a detector with a response time of 10 to 20 μsec should be used. This system is not sensitive enough to get a good clean Er decay and the system response time is over kill. There is a new detector available with the gain needed and a 10 to 20 μsec response time. This can be used to measure Er emissions in later studies.

The 1.6 μm emission from Pr was not obtained because the second order of the band gap was at the same spot in the spectrum. The system needs a 1 μm long pass filter to remove the band gap noise and allow the measurement of the 1.6 μm emission. The 1.1 μm emission was much weaker than the 1.38 μm emission and can be measured later with an improved system.

The follow-on to this effort should be to determine the effects of doping concentration, ion implantation energies and annealing time on the decay life times of the rare earth emissions. Additionally, perhaps an experiment to look at the effects

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of different kinds of doping could be done in the future. Diffusion doping could be tired because the equipment needed is minimal and the reported emissions from such samples are stronger than that by ion implantation. (14)

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13. ABSTRACT *(Maximum 200 words)*

Lifetime measurements of the excited states of three GaAs semi-conductors doped with the rare earth elements Erbium (Er), Praseodymium (Pr), and Thulium (Tm) has been studied using a pulsed nitrogen laser and germanium detector. The measurements were made with an experimental set up with a system response time of 0.34 usec. A 330 milliwatt nitrogen laser with a wavelength of 3370 A was used to excite intra $4f^n$ transitions of the rare earth elements. The rare earth impurities were implanted using ion implantation and and conventional annealing. The lifetimes of the excited states obtained were 361+ 58 μsec for the 1.54 μm Er emission, 40+7 μsec for the 1.39 μm Pr emission, and 8.7+0.8 μsec for the 1.23 μm Tm emission. The measurements for the Er are comparable to previously reported lifetimes. The TM and Pr lifetimes have not been previously reported. Of the three emission strengths, Tm was the strongest with Pr and Er being next in order.

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